Sampling and Analysis Plan 2005 for the University of Montana Watershed Health Clinic, Lakes & Reservoirs Project

I. Task 1: Lakes and Reservoirs

Task 1 General Description: Between June 2005 and September 2005, approximately 15 lakes and reservoirs will be sampled cooperatively by MT DEQ and the University of Montana Watershed Health Clinic. The lake-sampling crew chief will be hired directly by MT DEQ while the University of Montana Watershed Health Clinic will provide an assistant and some of the project supplies. Each waterbody will be sampled for chlorophyll a, total Kjeldahl Nitrogen (TKN), nitrate + nitrite (NO_{2/3}), total Phosphorus (TP), total dissolved solids (TDS), electrical conductivity (EC), temperature, and dissolved oxygen (DO). Candidate waterbodies are shown in Table 1.0 below; changes to the list of waterbodies may occur as a result of land access issues, etc., and will be approved by the MT DEQ prior to sampling. In addition, specific waterbodies will be sampled for additional water quality parameters as detailed in Table 1. Each waterbody will also receive an assessment of shoreline conditions following EMAP lake habitat protocols (EPA 1993).

Chlorophyll *a* samples will be analyzed in the laboratory of the University of Montana (U of M) Watershed Health Clinic; EC, temperature, and DO measurements will be made *in situ*; and TKN, NO_{2/3}, TP, TDS, EC, and all waterbody-specific parameters will be provided to and analyzed by the Environmental Laboratory of the MT Department of Public Health and Human Services (State Lab) in Helena, MT.

Water samples will be collected at one location midlake. An *in situ* DO and temperature profile, from surface to bottom, will be made to determine the extent of the epilimnion, thermocline, and hypolimnion. Equal volumes of water will be collected at each meter (starting from the surface) within a "zone of integration", defined as the photic zone of the epilimnion as determined by 3 times the Secchi depth, or to the depth of the thermocline, whichever is shallowest. In cases where the zone of integration is less than 3 meters deep, a water samples will be taken at the surface, middle, and bottom of the depth interval. Water samples from the zone of integration will be composited from discrete vertical point samples into a single carboy (therefore they are depth integrated).

Chlorophyll *a* will be sampled by filtering lake water unto GF/F filters, followed by freezing on dry ice or in a portable deep freeze. The vacuum on the filter shall be kept below 9.0 in. Hg to prevent cell rupture and loss of Chl *a* into the filtrate (Wetzel and Likens 1991). These filters will be analyzed within 30 days of collection, and will be corrected for phaeophytins. Samples for TKN, NO_{2/3} (which will first be filtered through 0.45 µm filter), TP, and TDS, and all waterbody-specific parameters will be preserved according to Standard Methods (APHA 1998) and/or DEQ SOPs and analyzed according to appropriate EPA methods. Sample replicates will be randomly taken on 10% of the total samples for each parameter except for chlorophyll *a*. Chlorophyll *a* will be collected in triplicate from each lake during each visit. Field blanks and filter blanks will be made on each sampling run and included with the samples, to evaluate contamination and detection levels under field conditions.

Table 1.0. Target lakes and reservoirs to be sampled in 2005.

Lake Name	LLID	HUC	COUNTY	LAT (dd)	LONG (dd)	ACRES	Special Sampling Instructions
Basin Creek Lake	1094287451454	10070006	CARBON	45.14536	-109.42862	6.3	Metals suite (drinking use) & common ions
Black Canyon Lake	1095330450697	10070006	CARBON	45.0695	-109.5330	79.3	Metals suite (drinking use) & common ions
Big Moose Lake	1097618450014	10070006	CARBON	45.0000	-109.7520	66.1	Metals suite (drinking use) & common ions
Rock Island Lake	1098100450156	10070006	PARK	45.01641	-109.80979	156.3	
Kersey Lake	1098404450280	10070006	PARK	45.02816	-109.84025	115.0	
Whitetail Reservoir	1122730460793	10020005	JEFFERSON	46.07926	-112.27295	602.8	Metals suite (drinking use) & common ions
Delmoe Lake	1123495459910	10020005	JEFFERSON	45.99096	-112.34959	279.1	
Clark Canyon Reservoir	1128823449691	10020001	BEAVERHEAD	44.96866	-112.91193	4815.1	Metals suite (drinking use) & common ions
Salmon Lake	1133980470875	17010203	MISSOULA	47.09145	-113.40061	631.3	Metals suite (drinking use) & common ions
Lake Alva	1135818473144	17010203	MISSOULA	47.3144	-113.58176	297.7	
Fishercap Lake	1136842487977	10010002	GLACIER	48.79761	-113.68411	12.7	
Redrock Lake	1137054487962	10010002	GLACIER	48.79638	-113.70534	26.4	
Lake Josephine	1136744487811	10010002	GLACIER	48.78194	-113.67295	130.3	
Mussigbrod Lake	1149136457831	10020004	BEAVERHEAD	45.79578	-113.61629	105.0	
Spar Lake	1155000484821	17010101	LINCOLN	48.26236	-115.94657	383.0	
							Metals suite (drinking use) &
Homestead Lake	1045674483920	10060006	SHERIDAN	48.39203	-104.56736	1199.29	common ions
Other Lakes/Reservoirs							
Lebo Lake (no access 2004)	1100329463135	10040201	WHEATLAND	46.31354	-110.0329	309.0	Metals suite (drinking use) & common ions
Tiber Reservoir	1111912483707	10030204	LIBERTY	48.3707	-111.19118	14842	(methylmercury only; near dam)
Mcgilvray Lake	1140798481429	17010208	FLATHEAD	48.14287	-114.07977	32.896	Metals suite (drinking use) & common ions

QA/QC plans for the field - U of M Watershed Health Clinic

Handling of water quality samples in the field

One 250 ml unfiltered sample will be kept in the dark on ice or in a refrigerator until analyzed for TDS and EC. Another 500 ml unfiltered sample will be preserved with H_2SO_4 to a pH < 2.0 and iced or refrigerated, for later analysis of TP and TKN. Sample bottles will be rinsed with lake water before collecting unfiltered samples.

Field filtration

For soluble nitrate + nitrite, 500 ml will be collected in wide mouth bottles, then filtered through a 0.45 um filter. 200 ml of filtrate will be placed in a HDPE bottle and frozen until analyzed, unless they can be sent to the State Lab within 48 hours of collection in which case they will be refrigerated only.

Filtration will be accomplished with a large syringe connected to a disposal filter capsule or a reusable filter holder. A small amount of deionized water followed by a small amount of the sample will be wasted through the filter before the filtered sample is collected. All reusable gear will be acid washed (10% HCl) and triple rinsed in deionized water between uses.

All sample bottles will be high-density polyethylene (HDPE). All sample bottles will be new or will be acid washed in 10% HCl & triple rinsed in deionized water. Samples bottles will be rinsed with a small amount of the filtered sample before collecting the final filtered sample.

Real-time measurement instrument calibration

The dissolved oxygen meter will be calibrated just prior to each sampling event using the 100% relative humidity calibration method. EC and temperature will be checked monthly in a laboratory environment and calibrated as needed.

Equipment to be provided by the MT Department of Environmental Quality

Some MT DEQ equipment for the Subtask 1.1 effort will be used cooperatively with the U of M Watershed Health Clinic for the 2005 field season. The MT DEQ will provide the items in Table 2 below:

Table 2. MT DEQ equipment to be used cooperatively with U of M, 2005. Number of items is followed by description.

- (1) 14' Jon boat w/ trailer 10 hp Mercury motor
- (1) Inflateable packable raft (Sea Eagle)
- (1) 12 V Electric trolling motor
- (3) Discrete Samplers (polycarb) & msngrs, and hand cables
- (1) YSI DO/temp/EC meter & Sonde w/ 100 ft cable

Anchor line and rope

- (1) Paristaltic pump 12v, field
- (2) 47 mm inline polycarb filter units for above
- (3) 12v deep cycle batteries
- (1) 12 v battery charger
- (1) First aid kit
- (1) Ring bouy, throwable
- (3) Life jackets
- (3) Ice chests
- (1) Sea Anchor
- (1) Toolbox and basic tools
- (1) hand-held GPS unit

QA/QC plans for the laboratory- U of M Watershed Health Clinic

Watershed Health Clinic protocols – chlorophyll, phaeophytin, AFDW

Chlorophyll/phaeophytin analysis

Filters will be allowed to thaw in their petri dishes at room temperature in the dark, removed from the petri dish and placed in a mortar. The samples will be ground for one minute in 95% ethanol alcohol using a pestle. Just enough solvent will be used to achieve a light green color (lab workers are trained to recognize the range of acceptable shades). The solvent is then drained into a small graduated cylinder and measured, and the solvent and sample are placed in a vial which is stored in the refrigerator. Once all the samples have been ground, the vials are warmed in a water bath to 75 degrees C and held there for 2 minutes. Then the chlorophyll extracts are centrifuged to clarity (absorbance at 750 nm < 0.01). Each vial of extract is handled in the following way: a 3ml aliquot of extract is removed from each vial, placed in a glass cuvette and read in a split beam, 2nm spectrophotometer at 664, 665 and 750 nm. Then the extract in the cuvette is acidified to 0.003M HCl (0.1ml of 0.1N HCL), mixed, held for 90 seconds and read again at the same wavelengths. Note: if the initial absorbance at 664 nm exceeds 0.8, the sample is diluted until absorbance is below 0.8. If absorbance at 750 nm is greater than 0.01 (or greater than 10% of the 664 reading), the sample is recentrifuged.

The amounts of pigments in the sample are calculated using the following formulae:

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Chlorophyll a in mg
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= DF x $[(A664b-A750b) - (A665a-A750a)] \times V \times [R/(R-1)] \times k / L$

Phaeophytin in mg

 $= DF \times R [(A665a-A750b) - (A664b-A750a)] \times V \times [R/(R-1)] \times k / L$

where A664b = absorbance at 664 nm before acidification

A665a = absorbance at 665 nm after acidification

R = acid correction ratio (maximum ratio of A664b:A665a,

i.e. for an extract containing no pheophytin) = 1.72

k = absorbance coefficient of chlorophyll a at 664 nm in 95% alcohol = 11.99

V = total volume of the extract in liters

L = length of the light path in cm

DF = dilution factor

After chlorophyll analysis is complete, the extracts are placed in aluminum weigh boats and dried for AFDW analysis.

QA/QC for the spectrophotometer:

The spectrophotometer is first zeroed against a blank of the same alcohol used for the extraction. Throughout the run the spec is checked against the blank to insure that there has been no drift. If the absorbance reading of the blank has drifted by more than 0.005, the spec is rezeroed. In addition, at the beginning of each run, an internal lab standard (a piece of clear green plastic) is read at 664,665,& 750 nm to determine that the spec is reading consistently from day to day.

The filters are thawed & transferred to aluminum weigh boats. Boats are dried to constant weight, stored in a dissector and weighed on an analytical balance. Then the samples & boats are ashed at 500 degrees C for an hour, cooled to room temperature, spritzed with water to rehydrate clays, dried again to constant weight, stored in a dissector and reweighed.

Ash free dry weight of the samples is computed by:

AFDW = dry weight – ashed weight.

REFERENCES

American Public Health Association. 1998. Standard methods for the examination of water and wastewater, 20th edition. American Public Health Association, Washington, D.C.

American Society of Agronomy. 1996. Methods of soils analysis part 3. Chemical methods. Soil Science Socity of America, Inc., Madison WI. Chapter 34. High temperature induction furnace method, pp 971-977.

Bahls, L. L. 2003. Algal indicators of nutrient availability in selected northeastern Montana streams June-August 2002. Prepared for MT Department of Environmental Quality under contract No. 200012-7.

Barbour, M.T., Gerritsen, J., Snyder, B.D., and J. B. Stribling. 1999. Rapid bioassessment protocols for use in streams and wadeable rivers: Periphyton, benthic macroinvertebrates and fish. 2nd edition. United State Environmental Protection Agency, EPA 841-B-99-002.

EPA. 1993. EMAP surface waters lake field operations volume I resource group manual. Environmental Monitoring and Assessment Program. Draft.

EPA. 2000. Nutrient criteria technical guidance manual, rivers and streams. United States Environmental Protection Agency, EPA-822-B-00-002.

EPA. 2002. Western Pilot Study: Field operations manual for wadable streams. Environmental Monitoring and Assessment Program (EMAP).

Solorzano, L., and J. H. Sharp. 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. Limnol. Oceanogr. **25**: 754-758.

Wetzel, R. G., and G. E. Likens. 1991. Limnological analyses, 2nd edition. Springer-Verlag.